3 Fluorination of All Enrichments of Uranium Oxides

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FLUORINATION OF ALL ENRICHMENTS OF URANIUM OXIDES*

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ABSTRACT

The equipment, operating procedures, and system characteristics, for a uranium oside touranium hexafluoride conversion facility for processing 20,000 Kg of U per year are described. Design of the flame-tower and associated subsystems, such as pneumatic unloading and transfer for oxide, feed screw and disperser for the tower, ash removal, filtering, cold trapping, and liquid UF_6 loading into cylinders, was dictated by the need for nuclearly safe geometry, so that all enrichments of uranium could be processed, and by the need for maximum protection of personnel from exposure to the uranium materials. Respiratory equipment is not required since the parts of the process, which are apt to allow release of airborne material, are additionally enclosed by glove boxes.

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INTRODUCTION

A facility has been built and operated by Goodyear Atomic Corporation at the Portsmouth diffusion plant for the production of UF_6 from all assays of purified uranium. The facility has the capability of processing purified uranium in its various oxide forms and as uranyl nitrate hexahydrate.

The prime criteria in designing the facility were that the system:

1. Must be able to process all enrichments of uranium oxide with safe geometry as the prime nuclear safety parameter,
2. Must provide for containment of alpha activity associated with all levels of uranium enrichment,
3. Must provide for strict conservation of the valuable uranium,
4. Should produce UF_6 at a minimum operating cost.

The facility was designed to produce 20,000 kilograms of uranium per year as UF_6. This design figure was based on a processing rate of 4 kilograms of uranium per hour, with allowances for maintenance and inventory down time, for a continuous 'I-day week operation.

The basic process is the direct fluorination of U_3O_8 with elemental fluorine in an air-cooled flame tower. The UF_6 in the off-gas stream is selectively frozen out in a -80°F cold trap. ' The traps are then heated and the UF_6 is drained as a liquid into 5-inch product cylinders. Off-gas from the cold traps flow through sodium fluoride traps (regenerated in situ) to bring the vent gas concentration below 5 ppm of uranium.

BACKGROUND

When the gaseous diffusion plant at Portsmouth was originally built, the decontamination and recovery building included a facility to convert uranium oxide to UF_6. This facility was designed to convert oxides, produced by a solution recovery system, to hexafluoride by use of stirred-bed, screw-type fluorination reactors. The magnitude of the operation initially was rather small -- production rates being approximately 100 kilograms uranium or less a month or 1200 kilograms uranium per year. The screw-type reactors, furthermore, were quite difficult to operate.

Development work, instituted in 1959 on an oxide fluorination tower, indicated that substantial savings would be possible if the screw-type reactors were replaced by a flame tower. As a result, the actual experimental tower was moved to the production area, was integrated with the existing UF_6 recovery system, and became the mode of oxide fluorination. The developmental tower, with minor modifications, was operated over the years to fluorinate Goodyear-generated oxide to UF,.

In 1964, Goodyear was designated to process to UF, all licensee and contractor purified uranium scrap returns above 10 percent assay. At that time, further minor modifications

to uprate the capacity of the flame tower were instituted. At the higher operating rates, it became apparent that the system assembled in 1959 was inadequate from several standpoints, and as a result of our accumulated operating experience, a proposal to design and build a new facility was submitted in late 1964.

The proposed system would solve the following basic problems inherent in our existing installation:

Handling Problems: All handling of solid uranium compounds was by hand. With the multiplicity of containers involved, this was a messy and manpower-consuming operation.

Health Physics Aspects: The handling problems led directly to Health Physics problems since the average assay of the licensee scrap material now processed was considerably higher than that formerly handled as a result of Portsmouth diffusion plant recovery operations. The sheer quantity of material being handled also was contributing to Health Physics problems; the point had been reached where respiratory protection was mandatory in the entire area when oxide conversion operations were being performed.

Discontinuity of Operation: The process as it existed was essentially a batch operation. The freeze-out of UF_6 was accomplished in six 5-inch cylinders in series. This arrangement meant that when the lead cylinder became full, it was necessary to shut down the system, remove the lead cylinder, move ail of the following cylinders up one position, and install a new cylinder in the sixth position. This limited the run-time and even under ideal conditions the equipment was onstream barely half of the time.

High Unit Costs: These first three problems led directly to high unit costs, and there was an excessive use of manpower for the amount of production attained.

Basically, the new design criteria required a system capable of handling fully-enriched materiai and for containing the material to prevent exposure of operating personnel. In the interest of operating economy, continuous UF_6 removal equipment and pneumatic powder handling systems were specified.

Approval for the new facility was received from the AEC in mid-1965 with construction and design engineering starting very shortly thereafter. The old system was shut down a year later *to* make the area ready for construction, and to facilitate future decontamination, a polyester resin floor topping was laid down over the entire area.

Much of the equipment installed in this new facility was fabricated by Goodyear, but a construction contractor installed the majority of the facility. In July, 1967, the construction contractor had completed his work and Goodyear maintenance forces finished installation of some of the final systems.

There was a considerable period of pre-operational testing and debugging of systems which extended to mid-November when the system was first operated.

Production rates of the facility have climbed steadily since initial start-up, and have attained the design production rate of 1200 kilograms of uranium per month on a basis of fifteen 8-hour shifts per week.

REACTIONS

The facility was designed to process returns of either uranyl nitrate hexahydrate or uranium oxide, hence a system to convert uranyl nitrate hexahydrate to U_3O_8 was included. The U_3O_8 produced from this system is fed, along with oxides received as such, to the fluorination system. The uranyl nitrate hexahydrate is converted to U_3O_8 in an electrically heated, rotary tube calciner. The uranyl nitrate crystals are first put into solution and then fed directly to the calciner tube. Sequentially, within the calciner tube, the solution first evaporates, the. UNH becomes molten, denitration occurs, and, in the final zone of the calciner, the material is reduced to U_3O_8.

Within the flame tower, the uranium oxides are fed through the top of the tower into an elemental fluorine atmosphere. There is a spontaneous flame reaction between the oxide and the elemental fluorine which produces UF_6 and oxygen. Feed rates of oxide to the tower are adjusted so that the wall temperature of the tower is maintained at approximately 1000°F. The fluorine feed is maintained so that there is approximately a 40 percent excess of fluorine. This excess of fluorine is maintained to prevent the formation of intermediate fluorides which can cause drastic plugging of the tower. The normal material balance across the tower is shown below:

$$U_3O_8 + 13\tfrac{1}{2}\ F_2 + (\text{air}) \rightarrow 3\ UF_6 + 4\ O_2 + 4\tfrac{1}{2}\ F_2 + (\text{air})$$

Tower Input	Tower Output	Cold-Trap Output
U_3O_8 - 4 kg U/hr	UF_6 - 13.4 scfh	UF_6 - 20-40 ppm
F_2 - 62 scfh	O_2 - 17.8 scfh	O_2 - 17.8 scfh
air - 8 scfh	F_2 - 20.5 scfh	F_2 - 20.5 scfh
	air - 8 scfh	air - 8 scfh

A certain amount of the oxide does not react during the first pass through the tower. This material is collected in an ash pot at the bottom of the tower and is subsequently pulverized and refed to the tower. The ash has a high uranium purity and it burns very well on refeeding. Most of the impurities in the oxide are filtered from the gas stream in a secondary disengagement section, This so-called filter ash, containing less than i percent uranium, is processed through solution recovery, rather than being refed to the tower system.

CALCINING SYSTEM

The UNH calcining system consists of a dissolver, storage columns, calciner, and calciner off-gas scrubber.

The dissolver is a 48-liter 5-inch slope tank. Uranyl nitrate crystals are introduced into the open upper end of the slope tank and water and acid are added to effect the solution. Recirculation of the solution is accomplished by an air-lift pump connected between the low end and the high end of the tank.

The storage system consists of three S-inch PVC columns and one 5-inch glass column, having a total capacity of 160 liters. This storage capacity allows dissolution of material on day-shift while providing enough solution to run the calciner system during the other two shifts.

The calciner is a Bartlett-Snow-Pacific electrically heated unit with a calciner tube $6\frac{3}{4}$ inches in diameter by 12 feet long; the furnace section is about $6\frac{1}{2}$ feet long and provides 3-zone temperature control with a maximum operating temperature of 2000°F. The final zone temperature is 1500°F. The furnace section of the calciner tube is made of centrifugally cast Thermalloy 40-B. Four stainless-steel rods rolling freely within the calciner tube keep encrustations from building up and act as a rod mill to keep the material powdered.

Solution is fed to the calciner via a packed column where the solution runs countercurrent to the gases being exhausted from the calciner. The feed solution scrubs the off-gases from the calciner and the off-gases preheat the feed solution. Operating conditions for the calciner are a normal feed rate of 10 liters per hour at a concentration of 200 grams uranium per liter. U_3O_8 produced by the calciner falls into a j-inch can for subsequent feeding to the fluorination system.

FLUORINATION SYSTEM

The fluorination system consists of several basic components.

A pneumatic handling system has the capability of transferring all solid uranium compounds to appropriate places within the system, including the feed hopper. The pneumatic system also includes a pulverizer.

The two tower feed hoppers, a system unto themselves, are designed to maintain a continuous supply of feed to the feed screw without interrupting the pressure integrity of the tower system. It is quite important that the pressure in the lower tower feed hopper be kept slightly above the tower pressure to prevent fluorine from backing into the uranium oxide.

The tower component includes a feed screw, which is driven by a closed-loop air motor, and a disperser assembly. The feed screw delivers the powder to the disperser cavity, and the disperser causes the uranium oxide to fall in a dispersed cloud into the top of the tower. The tower itself is a 5-inch diameter, longitudinally finned Monel pipe enclosed ir. an insulating jacket that is equipped with heaters to bring the system up to temperature before firing. Subsequent to firing, the heaters shut off and air, introduced at the bottom of the tower housing, flows across the fins to cool the reactor tower. Halfway down the tower is a disengagement section which causes the gas flowing in the system to do a 180° reversal of flow which effects a separation between the unburned oside and the gas stream containing UF_6 and light-weight impurities. At the bottom of the tower, an ash pot is pneumatically locked onto the tower and this pot receives the unburned solids.

A pair of filters is located downstream of the tower to remove any particulate matter that has not been disengaged from the gas stream. On these filters most of the oxide

impurities are trapped. Initially, these filters were a Monel mesh screen, but they are presently being converted to sintered metal filters.

A magnesium fluoride trap receives the gas stream leaving the filters to sorb volatile impurities.

Two -80°F cold traps are operated individually and give the capability of continuous UF_6 removal. The traps are Goodyear designed and built, and incorporate a unique approach to cold trap construction. Their egg crate filling becomes progressively finer from the inlet to the outlet of the trap. While this is a standard UF_6 cold trap design concept, the uniqueness comes from building the traps completely from aluminum rather than copper. The traps were fabricated by assembling 6-inch sections with the baffling welded into each section; sections were then welded together to form a 23-foot cold trap. The concentration of the gas entering the cold trap is between 20 percent and 30 percent UF_6 and the outlet gas concentration is 20-40 ppm uranium.

Regenerative sodium fluoride pellet traps remove any trace quantities of uranium from the off-gases from the cold traps.

An ionization instrument called a space recorder monitors the uranium concentration of the gas leaving the sodium fluoride traps. At this same monitoring point, a sample is run through a continuous SO_2-type fluorine analyzer, and the main gas stream is vented with an air jet as the prime mover.

An evacuation system consisting of four B-4 pumps is provided to purge and evacuate cylinder connections and other components associated with the tower. Two of these pumps, used for UF_6 evacuation, discharge back to the inlet of the cold traps; the other pair evacuates wet air through a sodium fluoride trap scrubber.

Pneumatic System

The pneumatic system performs several different functions:

1. Unloads oxide to the pulverizer feed hopper.
2. Transfers ash to the pulverizer feed hopper.
3. Grinds and transfers material in the pulverizer feed hopper to the tower feed hopper.
4. Grinds and transfers material in the pulverizer feed hopper to a can for removal from the system.
3. Serves as a vacuum cleaning system throughout the area.

The prime mover for the pneumatic system is a 285 cfm blower. Immediately ahead of the blower are eight S-inch × S-inch HEPA filters. Each material delivery point consists of a cyclone as well as a sintered metal roughing filter. The pulverizer incorporated in the system is a fluid energy mill and is completely integrated into the pneumatic system, All components of the pneumatic system are nuclearly safe on a geometry basis. One of the most difficult engineering and shakedown probiems was in obtaining a good, workable pneumatic system. The small size of the system,

coupled with the requiremer.t that it must be absolutely dust-tight, severely limited the companies interested in bidding on the system. In the final analysis, Goodyear did considerable modification work on this system after construction to improve its workability. The modifications were quite successful, and the system has since been highly reliable.

Tower Svstem

There are two feed hoppers on the tower system -- the upper and the lower feed hoppers. The upper feed hopper receives material from the pneumatic system and is subjected to whatever pressure is present in the pneumatic system. This hopper is connected to the lower feed hopper via two pneumatically operated ball valves. The lower feed hopper is buffered with air and maintained at a pressure very slightly above tower pressure. This differential is necessary to prevent back flow of fluorine. Excessive buffer pressure causes fluidization of the oxide and overfeeding of the tower. Transferring material from the upper hopper to the lower hopper without disturbing the lower hopper pressure is accomplished with the two ball valves which operate sequentially to lock the material from one hopper to the other. Capacitance level probes are utilized to actuate the ball valve system automatically and relieve the operator of continuously watching the feed level.

The helical feed screw, driven by an air motor, is mounted directly under the lower feed hopper. Air motor speed is read out pneumatically and transmitted to a control panel where a controller monitors the speed and controls the speed of the feed screw by automatically adjusting an air control valve.

The disperser on the tower functions to break up any agglomerations and to deliver a fine cloud of oxide into the flame tower. Maintaining a shaft seal is the major problem with the disperser. The seal presently being used incorporates a mechanical seal and a controlled air leak into the disperser section; the controlled air leak is mandatory to prevent fluorine from entering the disperser section which has limited heat sink capabilities.

As previously mentioned, the tower itself is a finned 5-inch Monel pipe with fluorine inlet lines at the extreme top of the tower so that flow of fluorine and oxide is concurrent. The reaction occurs at the top of the tower and the fins on the tower radiate the heat to the air. Thermocouples attached to the tower monitor temperatures.

Cold Traps

The cold traps are aluminum -- each is 22 feet *long* and 6 inches in internal diameter. The trapping temperature is -80°F, and liquefaction temperature is 200°F. An insulating shell, purged with dry air to prevent accumulation of water vapor and frost, is provided for the cold trap with the internal surface of the insulation serving as a vapor barrier, An annulus between the insulating shell and the trap is buffered with nitrogen, also to exclude wet air and frost.

When a trap becomes filled with UF_6, it is isolated from the system, the refrigeration is turned off, and electric heaters energized. The trap temperature is raised to 200°F which increases the associated pressure to 70 psia or better, depending upon the UF_6 purity level. Once the UF_6 is liquefied, it is drained into 5-inch cylinders for shipment to the diffusion cascade for re-feeding.

Sodium Fluoride Traps

The sodium fluoride traps are 5-inch heated and insulated Monel traps. Each trap takes a 55-pound charge of $-inch sodium fluoride pellets pretreated at 1000°F. Normal operating temperature of these traps is 225°F. The traps are regenerated by heating to 750°F, introducing bleed through the trap, and pumping the off-gas back to the inlet of the cold trap.

Glove Boxes

Certain parts of the facility have been enclosed in glove boxes which were installed where release of solid uranium compounds could be expected. As a result, the following operating segments were enclosed: oxide unloading booth; can loading booth; pulverizer compartment; upper tower section, including the feed screw and the disperser assembly; lower tower section, including the ash pot and the PG filters; and the pneumatic system HEPA filters.

All of the glove boxes are of stainless steel framing with Plexiglas panels. Inlet air to the glove box is filtered through a 20-micron sintered stainless steel sheet; exhaust air from the boxes passes through sintered stainless steel roughing filters, backed up by HEPA filters. There is a central manometer station where differential pressures and other significant pressures on each glove box can be read. Also, each glove box exhaust is monitored with an AIM-3 air radiation monitor. The output of these instruments is slaved to a control panel for central monitoring,

Health Physics Practices

The basic Health Physics criterion was that no respiratory protection would be required, except under unusual circumstances. The glove box procedures used in the facility are commensurate with the hazard from uranium alpha activity, but the stringency of our procedures does not approach that used in plutonium operations. Also, environmental AIM-3 radiation monitors located throughout the operating areas continuously read the radiation from airborne materiai. These monitors give operating personnel an immediate indication of any high airborne alpha activity. In addition to the continuously reading monitors, there are a number of eight-hour air samplers placed throughout the area which also provide a record of the airborne levels.

In the event one of the giove box systems must be opened or there is a leak in a non-contained system, activity is first detected by the AM-3 monitors. When conditions warrant, air hoods are used for respiratory protection; appropriate hook-up points for air hood hoses have been provided.

OPERATING PROBLEMS

Aside from the normal problems inherent with operating a fluorination system such as valve burnouts, etc., the two main problems are impurities in the oxide (leading to excessive filter plugging) and HF in the cold trap and sodium fluoride trap systems. The impurities are basically metal cations which fluorinate in the tower and form very lightweight fine particulate matter which carries through the tower disengagement section to the filters. Screen-type filters do not lend themselves to backblowing, and for this reason, sintered metal type filters are being installed. Backblowing sintered metal filters, however, must be done cautiously. Excessive introduction of air in the filter blowback procedure can cause sharp pressure fluctuations in the tower which, in turn, can lead to flow back of the fluorine into either the disperser cavity or the feed screw.

The HF problem causes high pressure in the cold traps when liquefying the UF_6 as well as the destruction of the absorptive capacity of the sodium fluoride pellets. HF is introduced into the system in small quantities from the fluorine and is formed, in larger quantities, from moisture contained in some of the oxides received. A secondary HF scrubbing system is presently being enlarged to obviate the HF problem on the incoming fluorine.

URANIUM CONTROL

A great deal of time and effort was expended in planning the uranium control procedures that would be used for this operation. A large number of small and various sized containers, containing uranium with wide assay variations, were expected as the source of feed. These containers would also pose a storage problem insofar as keeping enough feed on hand to sustain operations. Accurate records would be necessary of all uranium-bearing material generated in any form within the system. To facilitate uranium control, the following procedures were instituted:

1. A computer program was established to schedule feed into the facility so that assay mixing could be minimized, The computer produces a feed schedule as well as schedule cards and weight cards which accompany each shipment.
2. The materials handling group load the feed material according to the schedule onto a 12-container cart. The computer dictates the loading position on the cart so that the material can be removed in preferred order of feeding.
3. Each container has a schedule card and a weight card. The schedule card is appropriately marked to indicate when the material was fed to the system and then is returned to the Uranium Accounting group. The weight card contains information about the check weighing of the container and the check weighing of t'ne container tare weight, This information is also returned to Uranium Accounting.
4. A card is generated by the operators for every container of material produced by the system including UF_6, filter ash, tower ash, and any other uranium-bearing solids.

5. All of these cards flow to Uranium Accounting when the disposition of a container has been completed.

This system has minimized the problem of physically hunting for containers and the associated worry about the contents of each container.

CONCLUSION

The integrated oxide conversion facility was put into operation in November, 1967. Operation was started with low assay scrap and has been steadily progressing toward the fully enriched level. The capability of the system to produce material at the design rate has been proven.

Extrapolating alpha airborne activity data at our present assay levels to higher levels gives confidence that the containment systems and procedures will meet Health Physics standards.

Unit costs have not yet dropped to projected levels, the basic reasons being the **extra** start-up costs and modifications necessary to smooth out the system.

With reference to uranium losses, what could be considered as normal production losses are being developed; repeated operating periods and associated inventories are required before a **normal** operating loss can be established. The system is well monitored to obviate any real loss of material; nevertheless, holdup of uranium can occur within the system.